Energy, Mines and Resources Canada | Énergie, Mines et Ressources Canada

CANMET
Canada Centre for Mineral and Energy Technology | Centre canadien de la technologie des minéraux et de l'énergie

SULPHATION CAPACITY OF SWEDISH CARBONATE ROCKS

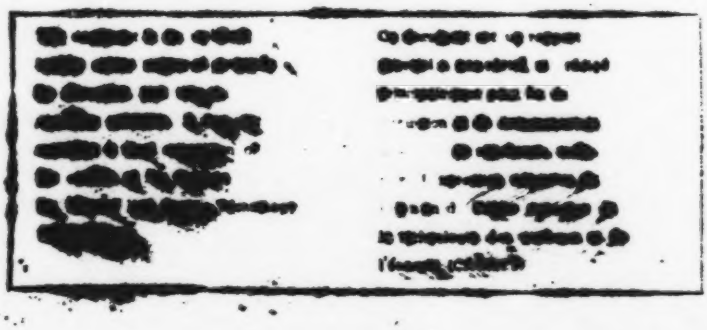
C.A. Hamer
Extractive Metallurgy Laboratory

September 1983

Project-ERP 4.3.4.1.01
Combustion and Emission Abatement Parameters

21 pp

MINERALS RESEARCH PROGRAM
MINERAL SCIENCES LABORATORIES
DIVISION REPORT ERP/MSL 83-121 (TR)



MICROMEDIA

SULPHATION CAPACITY OF SWEDISH CARBONATE ROCKS

by

C.A. Hamer

ABSTRACT

Eight carbonate rocks, which had been evaluated as SO_2 sorbents by the thermogravimetric analysis method at the Chalmers University of Technology, Göteborg, were evaluated at CANMET in a bench scale fluidized bed reactor. Although the absolute values of the sulphation capacity was different for the two methods, the reactor results being lower, the ranking of the carbonate rocks was identical. The Argonne National Laboratory model was used to predict the performance of the rocks as SO_2 sorbents in the 1MW fluidized bed combustor at the University of Göteborg.

CAPACITÉ DE SULFATATION DE ROCHES CARBONATÉES DE LA SUÈDE

par

C.A. Hamer

RÉSUMÉ

CANMET a évalué en laboratoire, dans un four à lit fluidisé, huit roches carbonatées que la Chalmers University of Technology (école polytechnique Chalmers) de Göteborg avait déjà évalué comme sorbant de SO_2 au moyen d'analyses thermogravimétriques. Bien qu'en valeurs absolues la capacité de sulfatation diffère selon la méthode utilisée, les résultats obtenus au moyen du four étant plus faibles, les rangs des roches carbonatées étaient identiques. Le modèle de l'Argonne National Laboratory (1) a été utilisé pour prédire le rendement des roches comme sorbant de SO_2 dans l'appareil de combustion en lit fluidisé de 1 MW de l'université de Göteborg.

(1) Illinois, États-Unis.

INTRODUCTION

Canada is a member of the International Energy Agency (IEA) Agreement for Co-operation in the Field of District Heating Boilers. The nine member nations share technical information and operating experience on AFBC. CANMET is the principal agency working on FBC in Canada. One project under its Energy Program is a study of Combustion and Emission Abatement Parameters, and one element of this project is an investigation on limestone utilization for SO_2 capture in AFBC. A number of Canadian limestones and dolomites have been evaluated in a bench scale fluidized bed reactor and also by thermogravimetry. These data have been used in the Argonne National Laboratory mathematical model to predict the performance of the limestones as SO_2 sorbents in AFBC (1). A similar study on the sulphation capacity of Swedish carbonate rocks by thermogravimetry was conducted at the Chalmers University of Technology, Göteborg (2). In the interest of comparing the evaluation technique for sorbents, the eight Swedish carbonate rocks were evaluated in the bench scale fluidized bed test reactor at CANMET. Also included in this test series were two samples of carbonates which had been received from Dr. E. Evenson, SINTEF, Norway, in 1982. These were from quarries which were also represented in the Chalmers samples. This report presents the results of those tests and the comparison with the Chalmers University results.

CHALMERS UNIVERSITY INVESTIGATION

The Chalmers University study was an in-depth investigation which encompassed chemical analysis, pore size distribution by mercury poresimetry, X-ray diffraction analysis, mineralogical examination of the stones, as well as attrition, calcination and sulphation experiments. This report will discuss only the sulphation results. The carbonate rock samples, limestone and dolomite, were obtained from seven quarries in Sweden. An eighth sample was made up by mixing an English dolomite with Linhamn limestone (Mg 5-50). Table 1 lists the samples and the calcium and magnesium contents.

Table 1 - Swedish Carbonate Rocks

Sample	% $CaCO_3$	% $MgCO_3$
Storugns	94.1	2.1
Linhamn	89.9	2.1
Mg 5-50	69.7	18.0
Ignaberga	91.1	1.0
Forsby	94.1	1.7
Orsa	96.2	1.0
Sala	62.4	37.4
Glanshammar	55.7	36.8
Linhamn	93.8	(Samples from Dr. Evenson,
Sala	54.5	Analysis by CANMET)

Experimental Procedure: Chalmers University

Three TGA tests were carried out on each rock sample:

a) particles sieved at 1-2 mm from the supplier's sample.

b) particles sieved at 0.125-0.25 mm from the supplier's sample.

c) particles sieved at 0.125-0.25 mm from crushed 1-2 mm particles.

The samples for sulphation testing were calcined for 2 h at 850°C in a rotary furnace. The calcination atmosphere was 15% CO_2, 85% N_2. In the sulphation test 50-100 mg of precalcined sample was placed in a Mettler thermobalance and brought up to 850°C in an atmosphere of 96% N_2, 4% O_2. After the sample weight had become constant, the atmosphere was changed to 0.3% SO_2, 4% O_2, 95.7% N_2 to sulphate the sample while constantly measuring the weight gain.

Experimental Procedure: CANMET

Sulphation tests were conducted in a bench scale fluidized bed reactor. The reactor is an externally heated stainless steel pipe, 53 mm diam by 1.4 m high, with a porous silica disc as a distributor located 350 mm from the bottom. For each test the reactor, with a bed of 250 g ASTM C109 silica sand fluidized by air, is heated to 850°C. The air is turned off and synthetic flue gas, 0.3% SO_2, 8% CO_2, 5% O_2, balance N_2, is admitted to the reactor. Ten grams of limestone, sieved at 0.842-1.000 mm, is injected into the fluidized bed. The SO_2 in the exhaust gas is continuously analysed by a Beckman Infrared Analyser. Within a minute

of adding the sample the SO_2 concentration in the exit gas drops to a fraction of the inlet concentration. It then begins to increase, the rate of increase being dependant upon the limestone, until after one to three hours the exhaust concentration is constant at or very near to the inlet concentration. As the area above this curve represents the SO_2 captured by the sorbent it is possible to calculate the per cent sulphation versus time for the sample. This sulphation curve is very similar to that obtained by the TGA method. A reiterative non-linear least squares computer program fits the following empirical equation to the sulphation data:

$$X(\%) = a[1-\exp(-kt^n)]$$

The parameters a, k and n are used for modelling. A more detailed description of this procedure is given in reference 1.

RESULTS

The sulphation curves for each of the samples are given as Fig. 1-8. The fluidized bed reactor data were added to the curves which had been photocopied from reference 2, consequently there will be some loss of accuracy in the reproduction. The maximum degree of conversion, or sulphation capacity, of the samples is given in Table 2.

Table 2 - Sulphation capacity Swedish carbonate rocks per cent conversion of $CaCO_3$ to $CaSO_4$

Sample	FB Reactor 0.841-1.00 mm	TGA series 1	2	3
Storugns	22.2	37.5	54.5	47.1
Linhamn	46.7	46.5	72.2	60.8
Mg 5-50	51.3	65.5	85.6	74.9
Ignaberga	23.0	55.6	14.6	58.4
Forsby	8.5	14.6	14.5	13.1
Orsa	15.3	28.0	46.5	37.0
Sala	12.7	19.4	16.1	16.5
Glanshammar	11.7	22.1	35.4	22.9
Linhamn*	37.2			
Sala*	8.3			

TGA data from Table 4, Reference 2
Series 1:1.00-2.00 mm, 2:0.125-0.250 mm, 3:0.125-0.250 mm (from crushed 1.0-2.0 mm rock)

*Samples from E. Evenson, SINTEF, Norway

The results in both the graphs and the table show that the sulphation capacity as determined by the fluidized bed reactor are generally much lower than determined by the TGA. The sulphation capacity of a sorbent generally increases with decreasing particle size so it would be expected that the fluidized bed sulphation results should be higher than that found for the 1.0-2.0 mm particles and lower than the 0.125-0.250 mm sizes. This is not the case; except for the Linhamn sample, the reactor results are all lower than those for the 1.0-2.0 mm size. Although the absolute values for the sulphation capacities are different, the ranking of the eight samples from best to worst sorbent is the same for both methods.

The sulphation capacity of the two rocks received from SINTEF do not agree very well with the material from the same quarries sampled by the Swedish researchers. Unfortunately the history of the samples is not known. This type of situation where samples from the same deposit have considerably varying sulphation capacities was also observed with Canadian samples. It is not surprising considering the heterogeneous nature of most carbonate deposits. The results emphasize the necessity of taking more than one sample in order to characterize a deposit. In practical terms it indicates the potentially changing nature of limestone feedstock to an AFBC over a time period.

That the sulphation capacities determined by the two methods are different is not surprising considering the different nature of the test procedures. In the TGA method the samples were precalcined at 850°C for two hours in a 15% CO_2 atmosphere. This treatment would promote the formation of an open pore structure with subsequent enhanced sulphation capacity (3). In the fluidized bed reactor the cold rock is injected into an 850°C bed of sand fluidized by a synthetic flue gas. It is subject to thermal shock decrepitation, simultaneous calcination and sulphation as well as attrition during the test run. Sample decrepitation may result in some loss of material due to eleutriation. The conditions to which the limestone is exposed are not condusive to optimizing its sulphation capacity. However, the fluidized bed reactor test more closely approximates the actual sulphation of limestone as it occurs in a fluidized bed combustor than does the TGA. One major difference between the test reactor and an actual combustor is the absence of coal ash in the reactor. There are indications that the sulphation behaviour may be influenced by the characteristics of the ash (4). Argonne National Laboratory reports

improved sulphation capacity in TGA when the limestone sample was mixed with coal ash. Preliminary tests by this author indicate the opposite effect, that is, replacing bed sand in the reactor with ash results in a reduced sulphation capacity for a limestone.

MODEL PREDICTIONS

Part of the Swedish investigation is to test these carbonate rocks in a 1MW boiler at the University of Göteborg. A description of this unit is given in reference 5. Unfortunately it did not provide all of the data required by model so that which was missing was estimated. The model being used is that of the Argonne National Laboratory and is detailed in reference 4. Its use is discussed in reference 1. Table 3 lists the fluidized bed operating conditions and Table 4 gives the sulphation curve equation parameters: a, k and n necessary for the model.

Table 3 - 1 MW AFBC University of Göteborg

Temperature = 850°C
Pressure - 101 kPa
Fluidizing velocity = 1.83 m/sec
Bed height at min fluidizing vel = 0.25 m
Bed height of fluidizing vel = 0.50 m (ref 5)
Bed area = 0.49 sq m (ref 5)
Number of openings in the distributor = 80 (ref 5)
Coal feed rate = 100 kg/h
Sulphur content in coal = 1%
Calcium content of sorbent = variable (ref 2)
Sorbent particle size = 0.95 mm
Sorbent particle density = 2.5 g/cc
Sorbent bulk density = variable (ref 2)

Table 4 - Sulphation curve parameters

Sample	a	k	n
Storugns	22.735	0.07361	0.8513
Linhamn	49.373	0.03641	1.0561
Mg 5-50	51.563	0.05385	0.8767
Ignaberga	23.584	0.08602	0.8463
Forsby	8.626	0.09399	0.9502
Orsa	15.501	0.09249	0.8934
Sala	12.986	0.18344	0.7892
Glanshammar	11.891	0.09702	1.0805
Linhamn*	37.192	0.05272	0.8750
Sala*	values out of range for computing		

TGA data from Table 4, Reference 2
Series 1:1.00-2.00 mm, 2:0.125-0.250 mm, 3:0.125-0.250 mm (from crushed 1.0-2.0 mm rock)
*Samples from E. Evenson, SINTEF, Norway

The model prediction for the performance of the Swedish carbonate rocks in the 1MW AFBC are given in Fig. 9 and 10. Fig. 9 shows the predicted sulphur retention versus the calcium:sulphur mole ratio. The Linhamn limestone and the Mg 5-50 mixture are superior sorbents. The Linhamn sample obtained from SINTEF is not quite as good as the Swedish one. Storugns and Ignaberga have practicaly identical performances and are only fair sorbents. The remaining sorbents have poor predicted performance. Fig. 10 gives the predicted performance from the practical viewpoint of the quantity of sorbent required versus sulphur retention. In this graph the two Linhamn samples bracket the Mg 5-50 mixture. The two dolomites, Sala and Glanshammar, and the Forsby limestone are very poor sorbents. This graph is based on a coal with 1% sulphur. If the sulphur content is a different value the quantity of sorbent required can be obtained by multiplying accordingly.

The model is useful in determining the relative ranking of sorbents as well as giving an indication of their expected performance. It does however have certain limitations which tend to result in the model over-predicting the quantity of sorbent required. It does not take into account the beneficial effects of recycling cyclone dust back to the bed. It assumes that all the sulphur capture occurs in the bed whereas in fact

some capture does occur in the freeboard. Although the model takes the bed particle size into account it assumes that the sulphation behaviour in the bed is the same as in the 0.841-1.000 mm particles used in the test. If the bed particle size is substantially different from the test size the model will be inaccurate.

CONCLUSIONS

Ten Swedish carbonate rocks were evaluated in the fluidized bed test reactor and compared with eight of the same samples tested by TGA at Chalmers University. The sulphation capacities as determined in the fluidized bed reactor were consistantly lower than those determined in the TGA. This difference is attributed to the different evaluation methods. However, the ranking of the sorbents based upon sulphation capacity was the same for both methods. A considerable difference was found in the Linhamn and Sala samples supplied by the Swedish researchers and by the SINTEF possibly indicating the heterogeneous nature of the carbonate deposits. The Argonne National Laboratory model was used to predict the performance of the carbonate rocks in the 1MW AFBC unit at University of Göteborg. It will be very interesting to compare the predicted results with the actual data from the 1MW trials when they become available. On the basis of the quantity of sorbent required for sulphur retention, the Linhamn limestone is considered to be the best material for FBC use.

REFERENCES

1. Hamer, C.A. "SO_2 sorbent utilization in fluidized beds"; Division Report ERP/MSL 83-6(IR); CANMET, Energy, Mines and Resources Canada; July 1983.
2. Anderson, E., et al. "Svenska karbonatstenars kapacitet att absorbera svaveldioxid vid atmosfarstryck"; Report A8201, Chalmers University of Technology, Göteborg, Sweden; 1982.
3. Ulerich, N.H., et al. "The influence of limestone calcination on the utilization of the sulphur sorbent in atmospheric pressure fluid-bed combustors"; EPRI FP-426, Project 720-1, Final Report; Aug. 1977.
4. Fee, D.C., et al. "Sulfur control in fluidized-bed combustors: methodology for predicting the performance of limestone and dolomite sorbents"; ANL/FE-80-10, Argonne National Laboratory, Illinois; 1980.
5. Morch, C.F. et al. "Operating experiences from a 1MW atmospheric fluidized bed"; Report A81-105, Chalmers University of Technology, Göteborg, Sweden, Mar 1981.

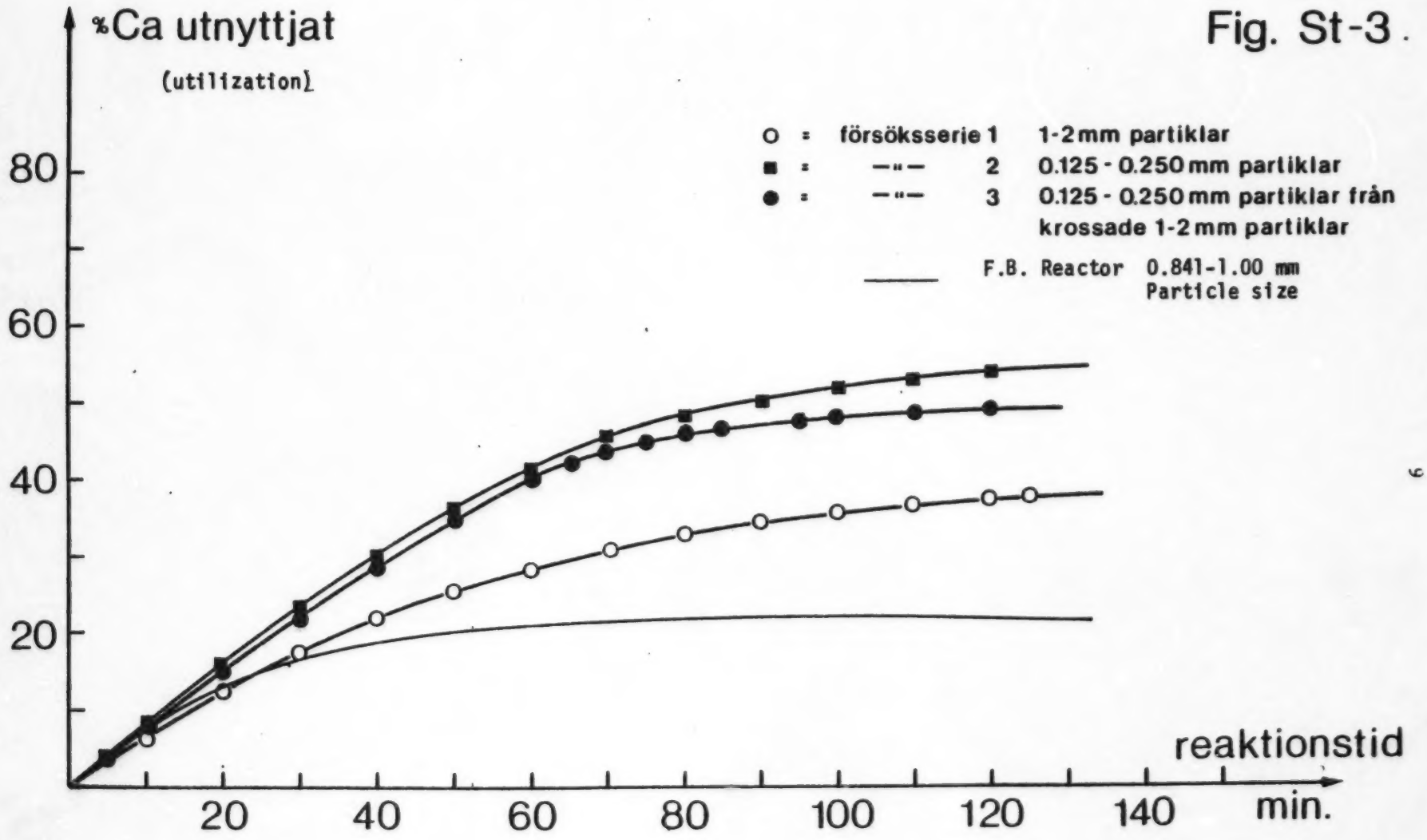


Fig. 1 - Sulphation curves for Storugns limestone

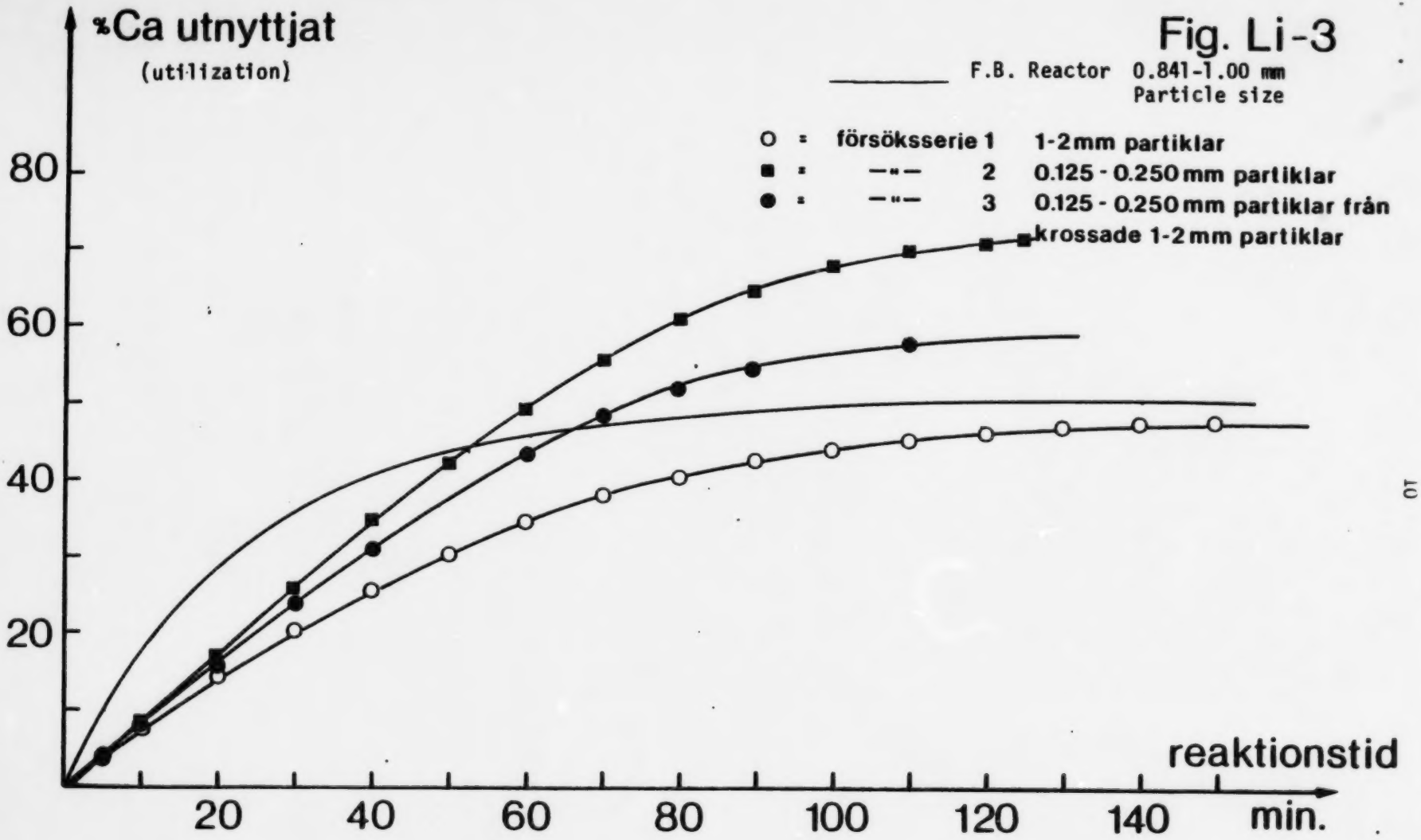


Fig. 2 - Sulphation curves for Linhamn limestone

Fig. LD-3

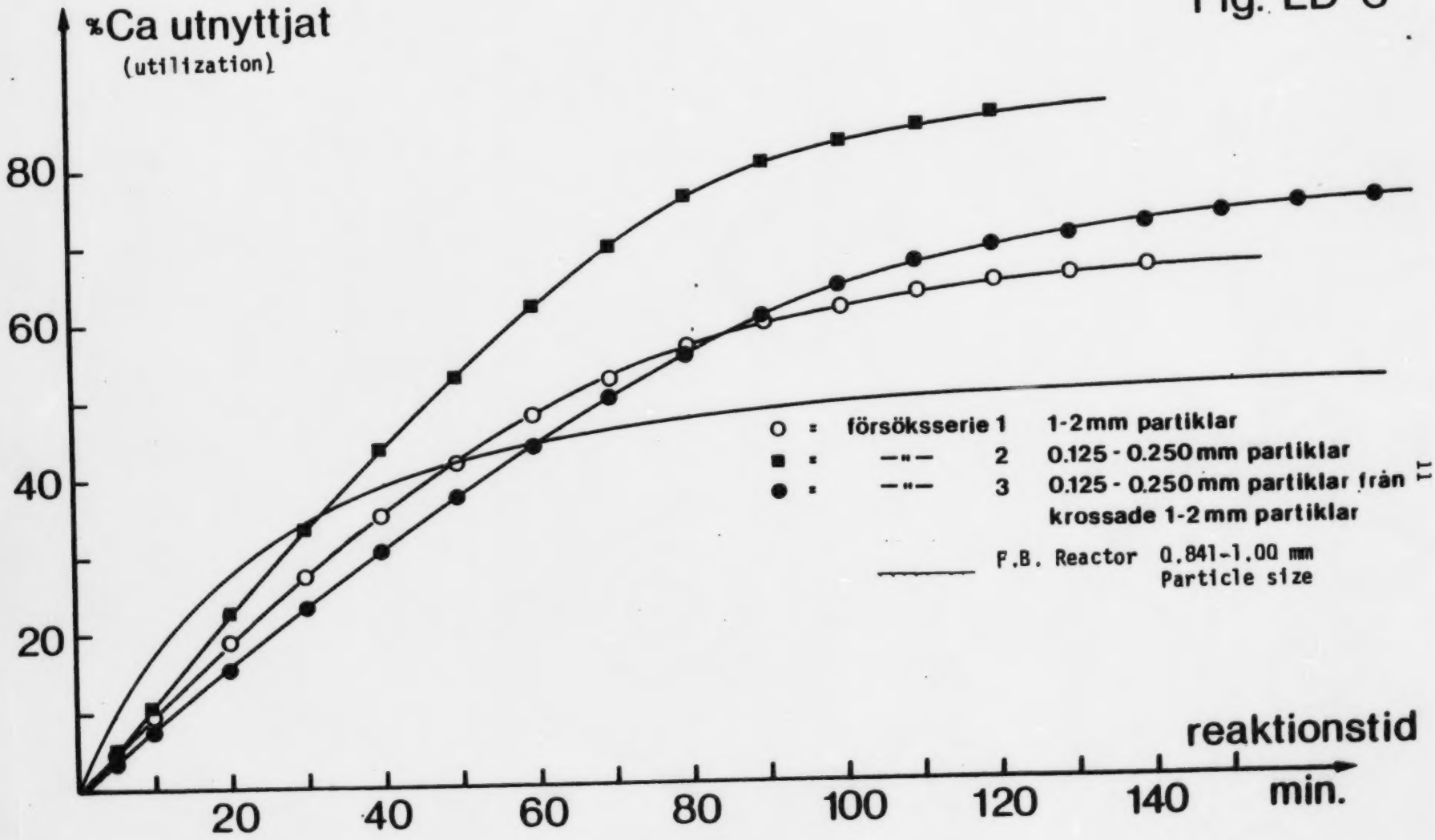


Fig. 3 - Sulphation curves for Mg 5-50 mixture of English dolomite and Linhamn limestone

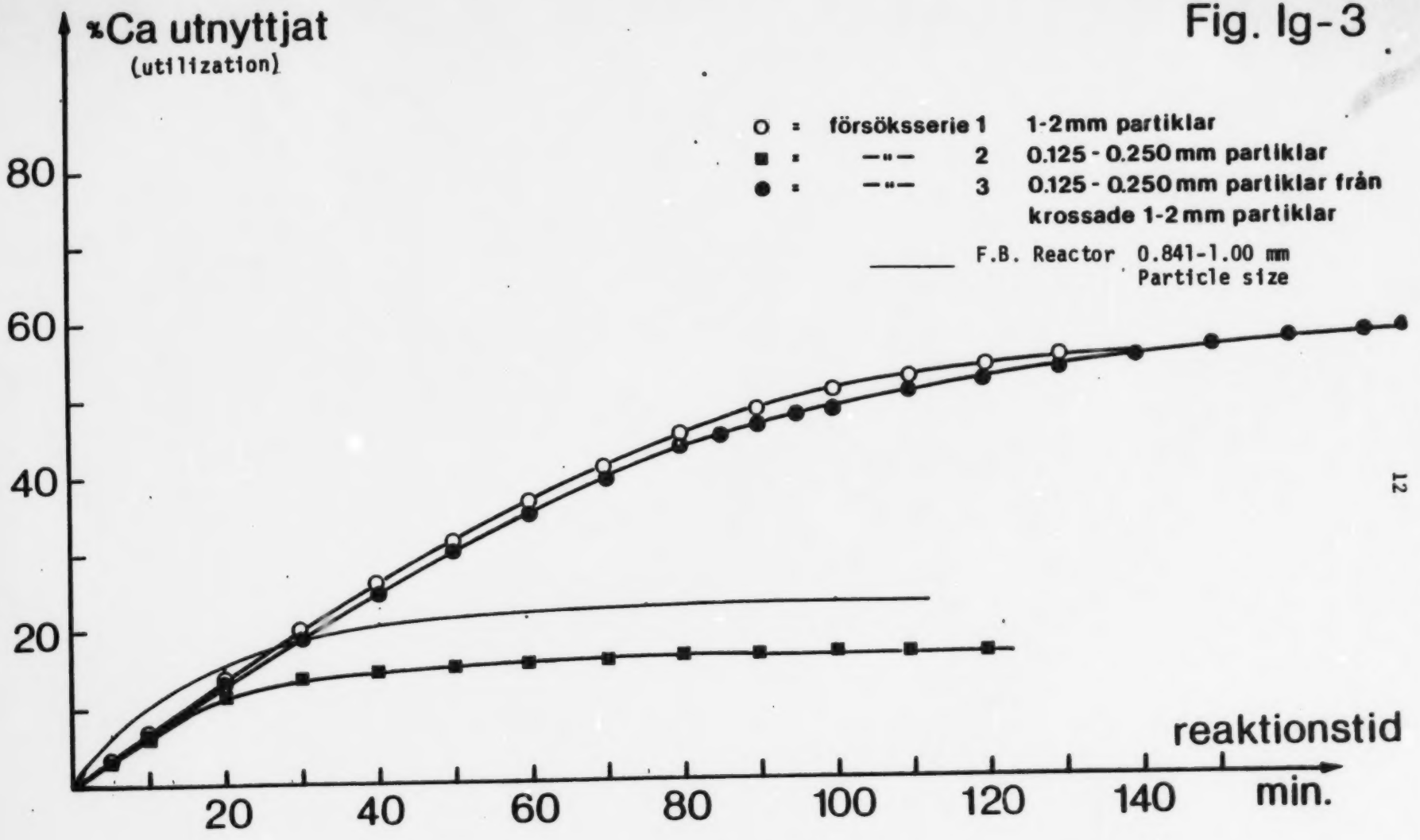


Fig. 4 - Sulphation curves for Ignaberga limestone

Fig. Fo-3

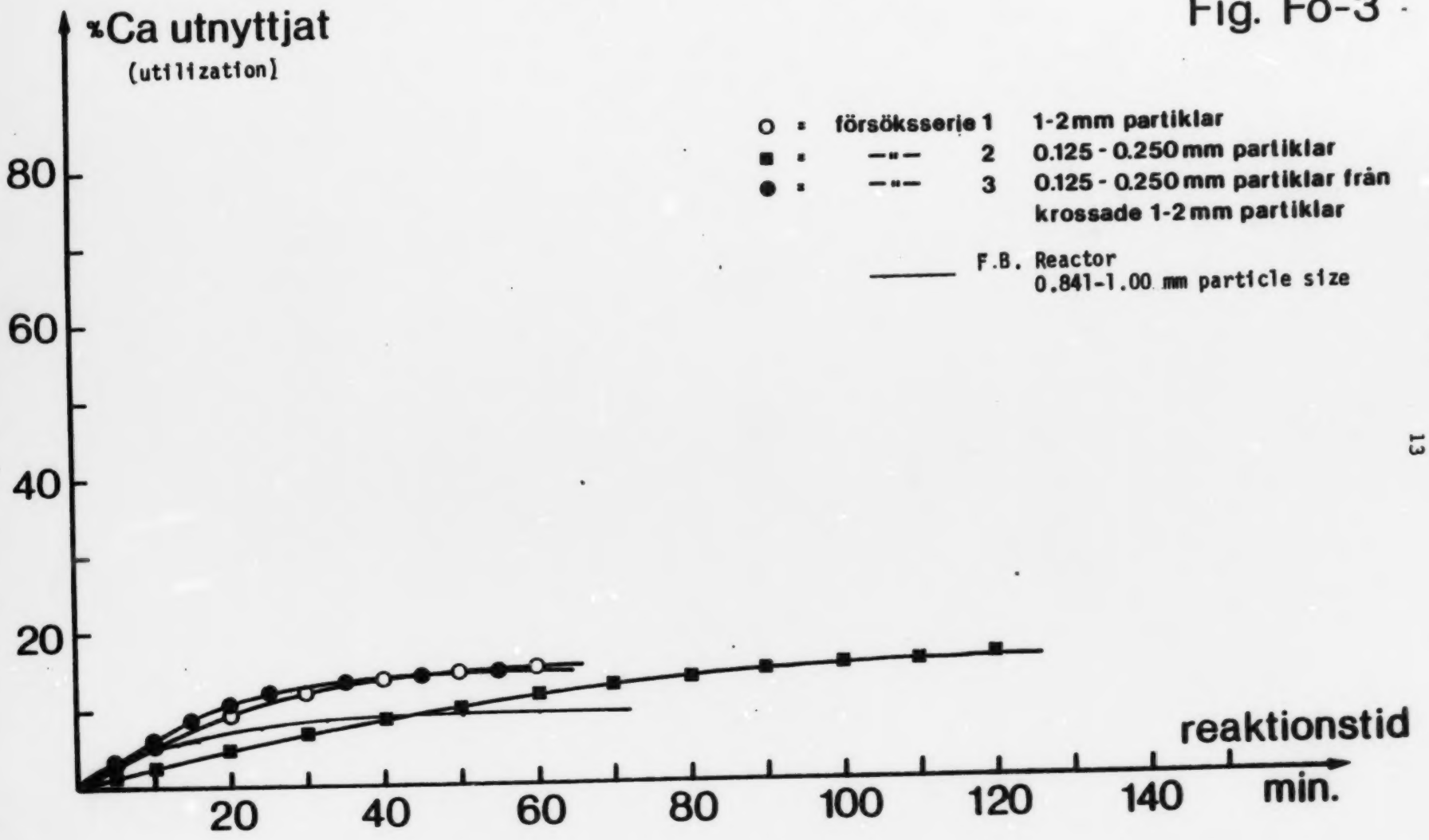


Fig. 5 - Sulphation curves for Forsby limestone

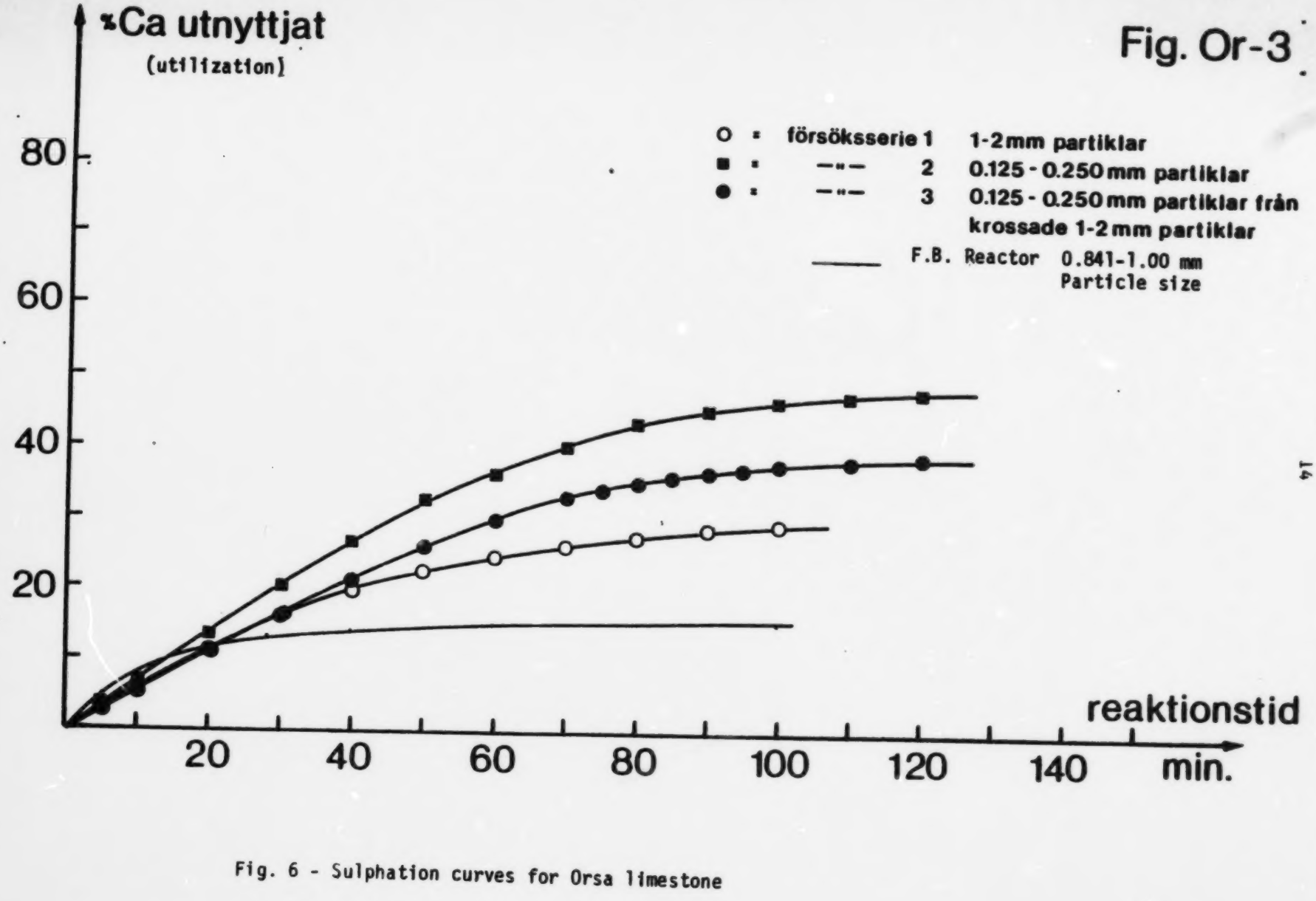


Fig. 6 - Sulphation curves for Orsa limestone

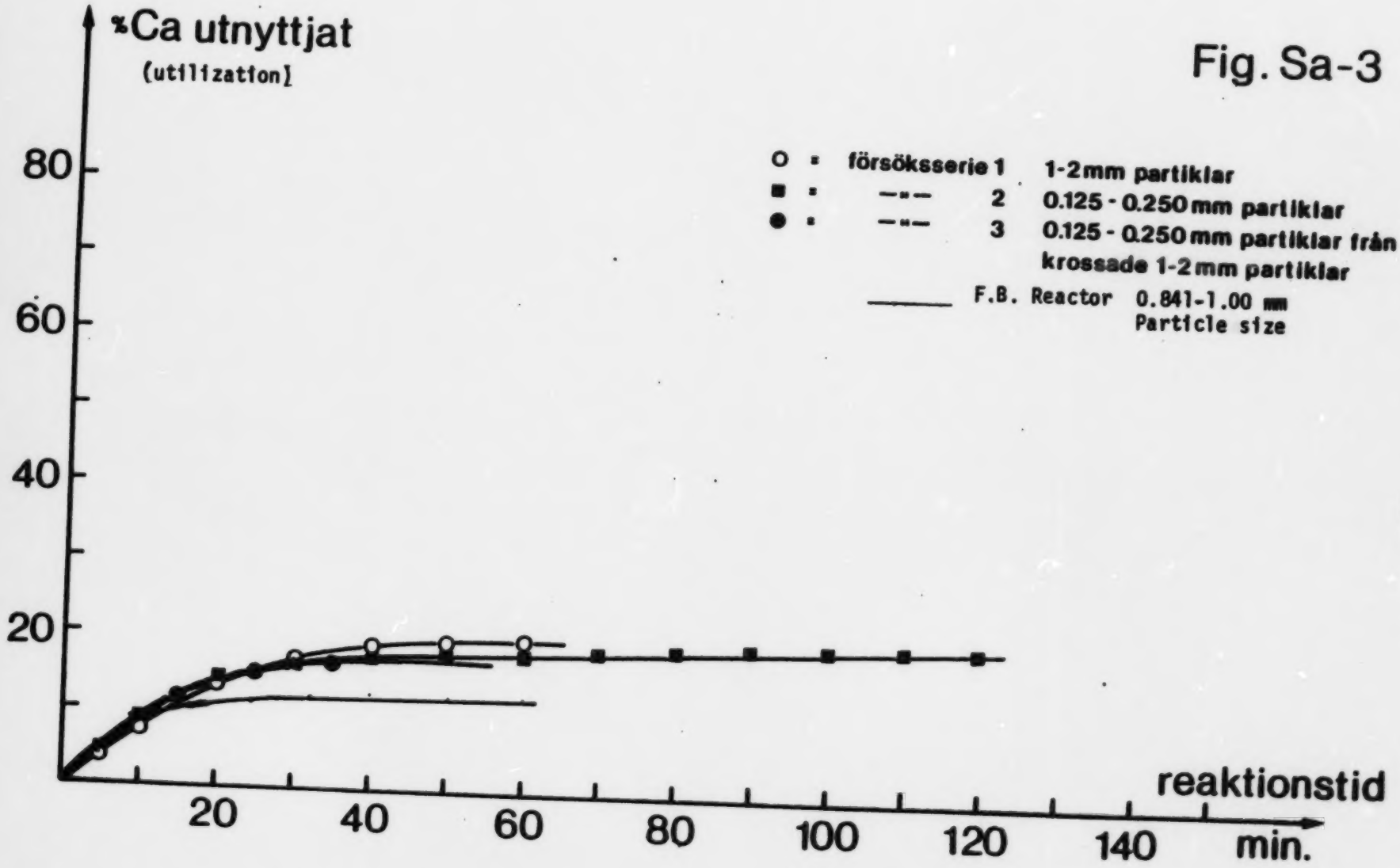


Fig. 7 - Sulphation curves for Sala dolomite

Fig. GI-3

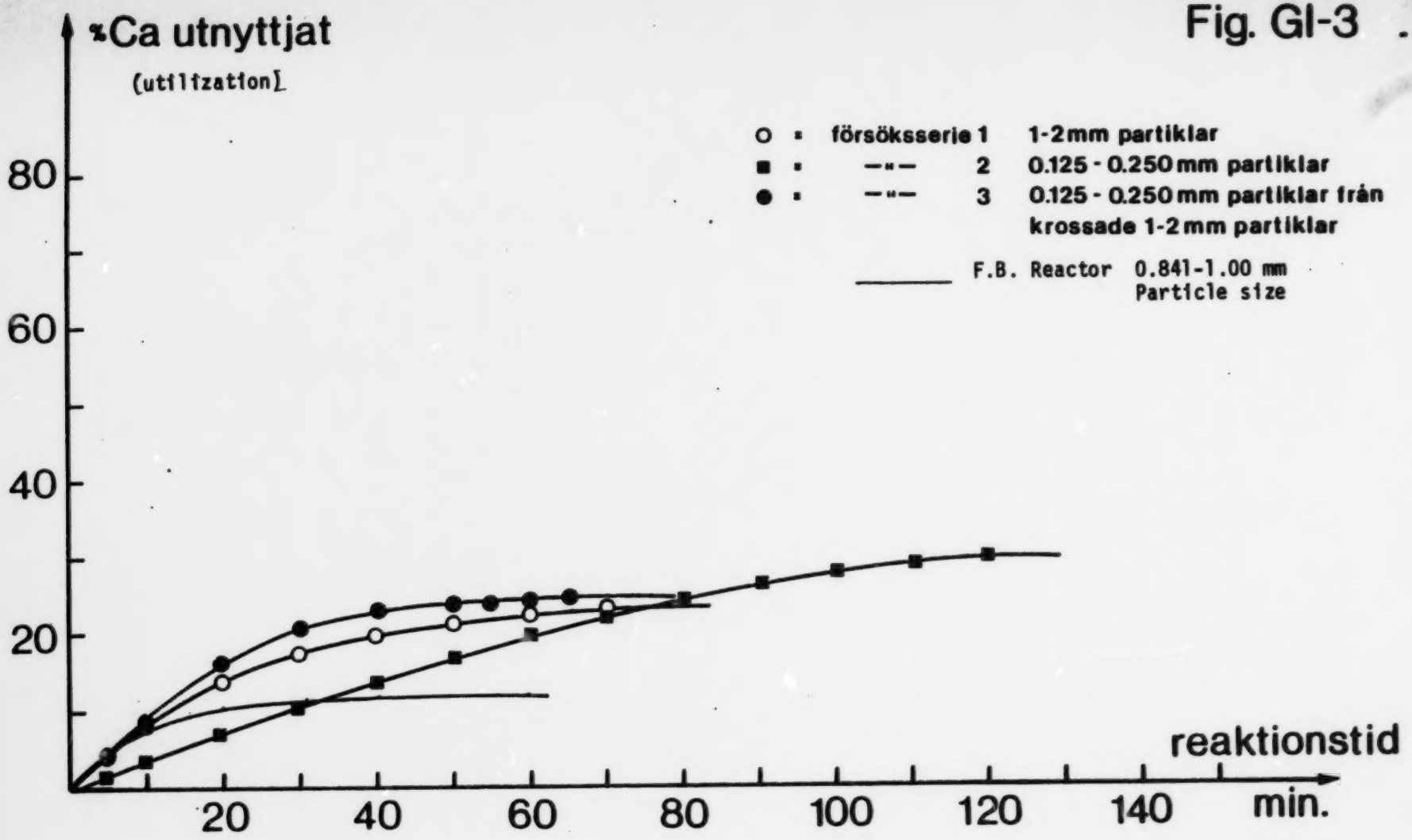


Fig. 8 - Sulphation curves for Glanshammer dolomite

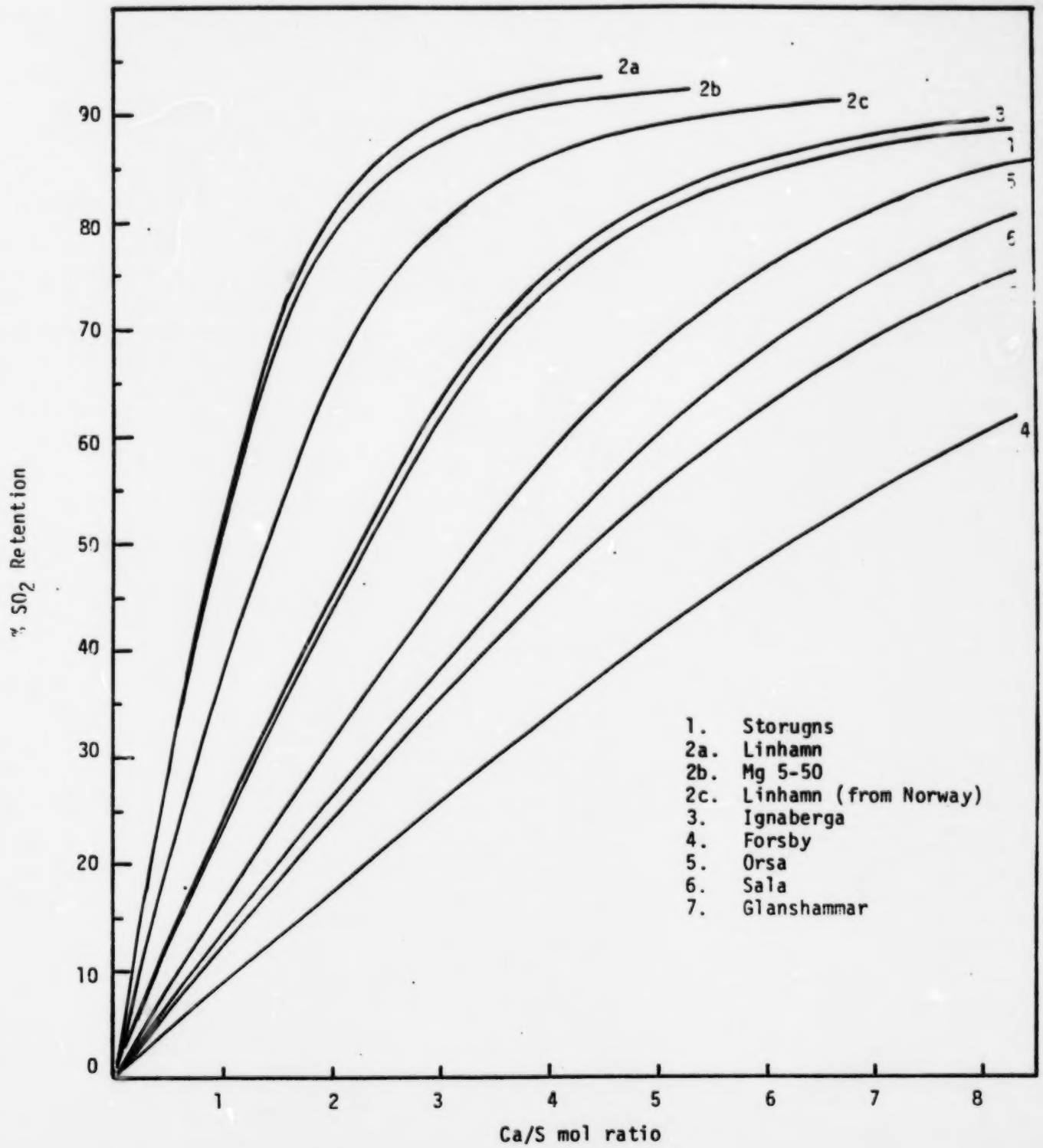


Fig. 9 - Predicted performance of Swedish carbonate rocks in the Goteborg 1 MV AFBC

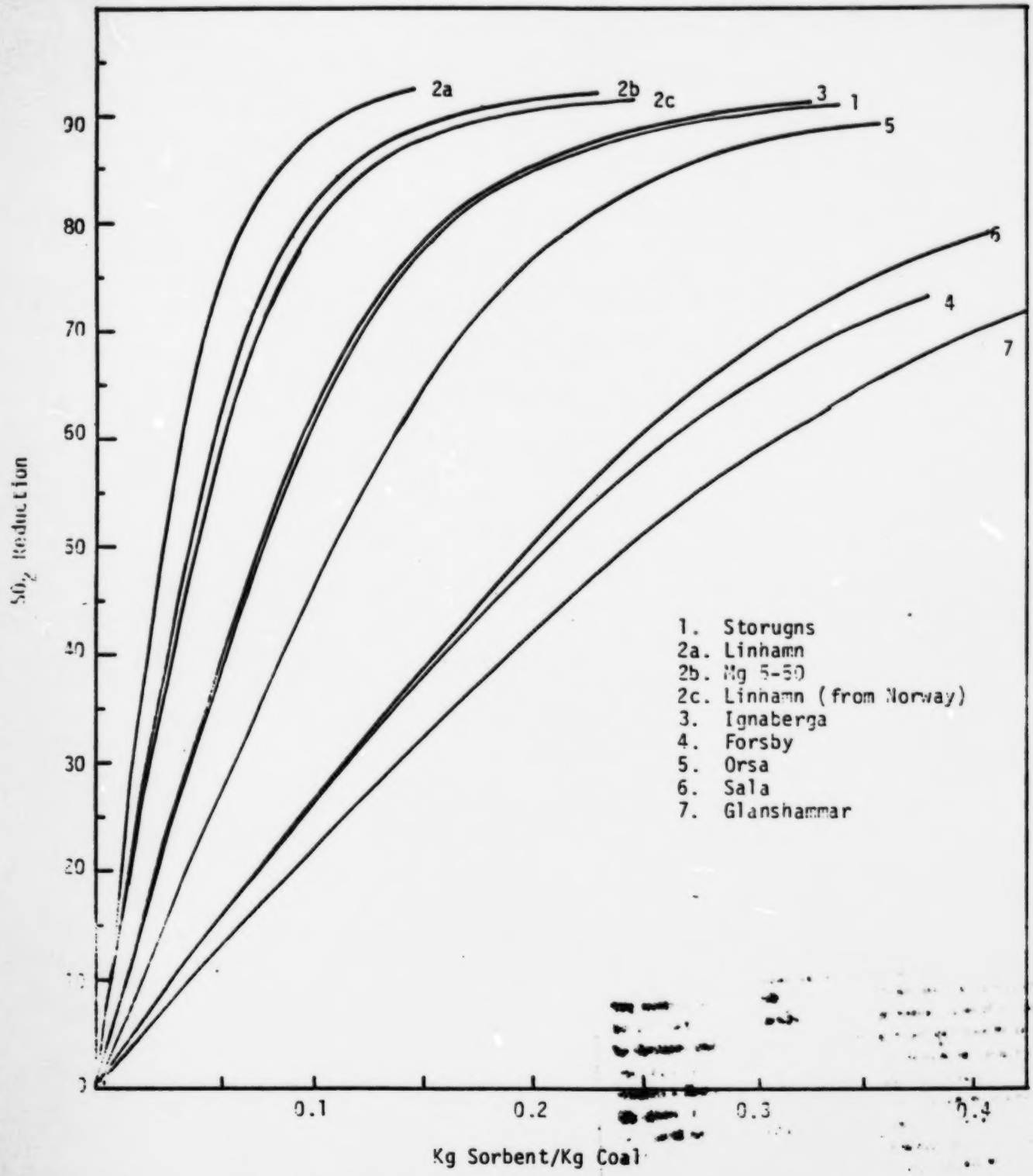


Fig. 10 - Predicted quantity of Swedish carbonate rock required for the Goteborg 1 MW AFBC combusting 1% S coal.